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Figure 1: Fig. 1. Infrared spectrum of dinaphthylamine

Abstract

Full Text

PHYSICAL CHEMISTRY

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INFRARED SPECTRA OF SOME SECONDARY AROMATIC AMINES

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Secondary aromatic amines are of great importance in the chemical industry as inhibitors used as additives to rubbers in rubber mixtures.

Meanwhile, no systematic study has been made of the relationship between structure and vibrational spectra in secondary amines. In Colthup' s review (ˆ1), where, along with other aromatic compounds, aliphatic and aliphatic-aromatic amines are considered, it is mentioned that secondary amines have intense absorption bands in the regions 1200-1300 and 3600-3500 cmˆ−1, which the author assigns to the stretching vibrations of the C—N and N—H bonds, respectively.

Fig. 1. Infrared spectrum of dinaphthylamine

In Bellamy' s monograph (ˆ2) it is also noted that all secondary amines in dilute solutions have one band in the 3200-3500 cmˆ−1 region, while at higher concentrations, owing to hydrogen bonding, a second absorption band appears on the long-wavelength side. For the absorption band of the stretching vibration of the C—N bond the region 1280-1350 cmˆ−1 is given. These works, as well as a number of others, discuss the position of the absorption band of the out-of-plane deformation vibration of the N—H bond. In secondary amines the absorption band of this vibration is of low intensity; it is assumed that it should appear in the region 1480-1650 cmˆ−1, i.e., in the same region as the characteristic band for the in-plane deformation vibration of the C—H bond (ˆ3). In other works (^{4,}5), individual portions of the spectrum of diphenylamine are considered. Thus, the literature contains no complete consideration of the vibrational spectra of secondary aromatic amines, nor complete infrared absorption spectra. As for tetraphenylhydrazine, the literature contains no information about its vibrational spectrum.

In the present work, a study was made of the infrared absorption spectra of diphenylamine, dinaphthylamine, β-naphthyl-N-phenylamine, and tetraphenylhydrazine in the region 4000-3700 cm^−1.

Before recording, the aromatic amines were purified by repeated recrystallization. Tetraphenylhydrazine was obtained from diphenylamine

···by the method described in the literature (9). The infrared absorption spectra of all the substances studied were obtained in the solid phase by depositing from solution onto a KBr plate. The spectra of the amines and tetraphenylhydrazine were recorded on an IKS-11 infrared spectrograph. The infrared spectrum of tetraphenylhydrazine was also obtained at 100° in a thermostated cuvette. The following slits were used:

Prism	Frequency interval, cm^{-1}	Spectral width, cm^{-1}
KBr	450—500	6
KBr	500—700	5
NaCl	650—800	4
NaCl	760—1075	5
NaCl	990—1340	7
NaCl	1300—1500	9
NaCl	1500—1600	11
NaCl	1600—1750	13
NaCl	1700—3500	16
LiF	2300—3500	8

The frequencies of the infrared absorption bands obtained are summarized in Table 1. The spectra obtained contain characteristic bands of the amines, as well as of the phenyl and β-naphthyl radicals, respectively.

In the region of the stretching vibration of the N—H bond, all the amines have two absorption bands: for dinaphthylamine, 3425 and 3465 cm^{-1}; for β-naphthyl-N-

Table 1

Dinaphthylamine ν, cm^{-1}	Dinaphthylamine intensity*	β-Naphthyl-N-phenylamine ν, cm^{-1}	β-Naphthyl-N-phenylamine intensity	Diphenylamine ν, cm^{-1}	Diphenylamine intensity	Tetraphenylhydrazine ν, cm^{-1}	Tetraphenylhydrazine intensity
475	weak	460	weak	460	weak		
		485	weak	485	weak		
		615	weak				
		658	weak	645	weak		

Dinaphthylamine ν, cm^{-1}	Dinaphthylamine intensity*	β-Naphthyl-N-phenylamine ν, cm^{-1}	β-Naphthyl-N-phenylamine intensity	Diphenylamine ν, cm^{-1}	Diphenylamine intensity	Tetraphenylhydrazine ν, cm^{-1}	Tetraphenylhydrazine intensity
		690	very strong	691	very strong	690	very strong
				701	medium		
736	very strong	735	very strong	735	very strong	740	very strong
806	very strong	820	medium				
851	very strong						
880	strong	860	strong	880	strong		
		885	weak				
		915	weak				
968	weak	960	weak				
				1002	weak	1008	weak
1040	weak	1020	weak	1038	weak	1040	weak
1070	weak	1080	weak	1086	weak	1000	weak
1115	weak	1115	weak	1098	weak		
		1130	weak				
		1168	weak	1162	weak	1160	weak
				1172	weak	1178	weak
				1188	weak		
1235	weak	1215	weak	1225	weak	1208	weak
		1238	weak	1240	weak		
		1260	very strong	1298	very strong	1250	strong
1280	strong	1276	very strong	1312	very strong	1275	very strong
						1300	strong
1380	weak						
1400	weak	1400	weak	1425	medium	1420	medium
1450	weak	1460	medium	1459	medium		
				1405	strong	1495	very strong
1515	very strong	1500	very strong	1520	very strong		
1535	very strong	1535	weak				
		1550	weak				

Infrared spectrum of β-naphthyl-N-phenylamine

Figure 2: Infrared spectrum of β-naphthyl-N-phenylamine

Dinaphthylamine ν, cm^{-1}	Dinaphthylamine intensity*	β-Naphthyl-N-phenylamine ν, cm^{-1}	β-Naphthyl-N-phenylamine intensity	Diphenylamine ν, cm^{-1}	Diphenylamine intensity	Tetraphenylhydrazine ν, cm^{-1}	Tetraphenylhydrazine intensity
1562	very strong	1562	weak				
		1598	very strong	1599	very strong	1598	very strong
1615	medium	1620	strong				
1650	weak						
1700	weak						
1750	weak						
1775	weak						
3060	weak	3060	medium	3050	weak	3085	weak
		3085	strong	3074	strong		
3425	weak	3430	medium	3392	strong		
3435	strong	3450	strong	3430	strong		

* Band intensity: weak —weak, medium —medium, strong —strong, very strong —very strong.

aniline: 3430 and 3450 cm(^{-1}), and for diphenylamine: 3392 and 3430 cm(^{-1}), the shorter-wavelength band in all the amines being more intense than the longer-wavelength one. Apparently, the longer-wavelength band arises due to intermolecular hydrogen bonding of the amino hydrogen, while the shorter-wavelength band belongs to the stretching vibration of the N—H bond. Naturally, in tetraphenylhydrazine no absorption bands are observed in this region. As might have been expected, in the region 3050—3085 cm(^{-1}) all the amines have intense absorption bands, which undoubtedly belong to the stretching vibration of aromatic C—H bonds. In diphenylamine and β-naphthyl-*N*-phenylamine, on the long-wavelength side there is also another band, which is possibly explained by splitting of the frequency in connection with intermolecular interactions occurring in the solid phase.

Fig. 2. Infrared spectrum of β-naphthyl-*N*-phenylamine

In all the amines and in tetraphenylhydrazine, intense absorption bands are present in the region 1200—1300 cm(^{-1}), which apparently belong to the stretching vibration of C—N bonds. However, it should be noted that if dinaphthylamine has one band with a frequency of 1280 cm(^{-1}), then β-naphthyl-*N*-

Infrared spectrum of diphenylamine

Figure 3: Infrared spectrum of diphenylamine

phenylamine and diphenylamine have two bands each (1260, 1276 and 1298, 1312 cm(^{-1}), respectively). Tetraphenylhydrazine has three absorption bands in this region (1250, 1275, and 1300 cm(^{-1})). Apparently one of them (probably the 1300 cm(^{-1}) band) belongs to the stretching vibration of the N—N bond, although for this vibration in the case of hydrazine the band 850 cm(^{-1}) is assigned ((^6)). As can be seen from Table 1, we have no bands with such a frequency. It is known that tetraphenylhydrazine at temperatures above 70° readily decomposes, giving free diphenylazotyl radicals. Evidently, upon decomposition of the molecule, the intensity of the absorption band of the stretching vibration of the N—N bond should decrease. Indeed, the infrared absorption spectrum of tetraphenylhydrazine obtained at 100° (Fig. 4, dotted curve) shows a sharp decrease in the intensity of the 1300 cm(^{-1}) absorption band, whereas the bands at 1250 and 1275 cm(^{-1}) merge into one. Other regions of the spectrum show no substantial changes. The bands at 1250 and 1275 cm(^{-1}) apparently belong to the symmetric and antisymmetric stretching vibrations of C—N bonds. Incidentally, in two of the three amines studied, in the region 1200—1300 cm(^{-1}) there are two bands each, which, apparently, could also be assigned to the symmetric and antisymmetric vibrations of the C—N bonds. It does not seem possible to assign any band unambiguously to the in-plane deformation vibration of the N—H bond. When comparing the absorption bands of diphenylamine and tetraphenylhydrazine, it is not difficult to see that the bands at 1459 and 1520 cm(^{-1}) of diphenylamine disappear on going to tetraphenylhydrazine. The frequencies 1450 cm(^{-1}) in dinaphthylamine and 1460 cm(^{-1}) in β-naphthyl-N-phenylamine are very close to one of the above-mentioned frequencies (to 1459 cm(^{-1})) of diphenylamine. These bands could tentatively be assigned to the in-plane deformation vibration of the N—H bonds in amines. Out-of-plane deformation vibrations of the N—H and C—H bonds fall in the region 700–1000 cm(^{-1}). From the data obtained it is not difficult to see that in this region, in addition to the band belonging to the vibrations of the C—H bonds of the phenyl and naphthyl radicals, all the amines have intense bands (860–880 cm(^{-1})), while tetraphenylhydrazine has no band in this region, which once again supports our supposition. These bands, apparently, belong to out-of-plane deformation vibrations of the N—H bond. In symmetrical amines (i.e., in naphthylamine and diphenylamine) the frequencies of these bands are the same (880 cm(^{-1})), while in β-naphthyl-N-phenylamine it is somewhat lowered (860 cm(^{-1})). The remaining bands may be assigned to various vibrations of the phenyl and β-naphthyl radicals.

Fig. 3. Infrared spectrum of diphenylamine

Fig. 4. Infrared spectrum of tetraphenylhydrazine

Fig. 4. Infrared spectrum of tetraphenylhydrazine

Figure 4: Fig. 4. Infrared spectrum of tetraphenylhydrazine

The intense bands at 690, 740, 1495, and 1598 cm(^{-1}) in tetraphenylhydrazine undoubtedly belong to various vibrations of the phenyl group ((^1)). Very close in frequency and intensity are the bands of the phenyl group (691, 735, 1495, and 1599 cm(^{-1})) present in diphenylamine. In considering the bands of dinaphthylamine it is not difficult to note the characteristic absorption bands of the β-naphthyl ((^7)) radical, namely: 736, 806, and 851 cm(^{-1}); the remaining intense bands (1515, 1535, 1562, 1615, and 1650 cm(^{-1})) are characteristic ((^8)) of the naphthalene skeleton. The spectrum of β-naphthyl-N-phenylamine has absorption bands characteristic both of the phenyl and of the naphthyl radicals.

Thus, consideration of the infrared absorption spectra obtained makes it possible to establish a certain correspondence between the structure and the vibrational spectra of secondary aromatic amines.

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